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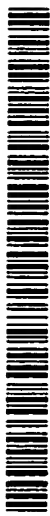
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(54) Title: SLURRY FOR FORMING INSOLUBLE SILICATE DURING CHEMICAL-MECHANICAL POLISHING

(57) Abstract: An aqueous slurry for chemical-mechanical polishing of silica substrates comprising: water, submicron abrasive particles, and a silica protecting agent having a solubility in water of less than 0.01 g/100 mL. The silica protecting agent is selected from alumina and zirconia.

5 SLURRY FOR FORMING INSOLUBLE SILICATE DURING CHEMICAL-  
MECHANICAL POLISHING

The invention relates to a slurry for minimizing or lowering oxide removal from silica surfaces during chemical-mechanical polishing, CMP, especially for polishing  
10 substrates containing smaller and higher density features.

US Patent 5,476,909 discloses a known aqueous slurry for CMP polishing of a semiconductor substrate having a composite of silica and a metal comprising, comprising: water and submicron abrasive particles. The slurry further has a compound which suppresses the rate of removal of silica.

15        One problem prevalent throughout the polishing industry is the unwanted removal of silica from the substrate during polishing, known as, erosion. The features on silica substrates are decreasing in size and the density of features on silica substrates is increasing. Thus, it is becoming more and more important to protect the silica surface in order to minimize inconsistencies in the polished substrate.

20 It is thus desirable to provide a polishing slurry that protects the silica surface while still providing acceptable metal removal rates.

According to the invention, an aqueous slurry is provided which is useful for the chemical-mechanical polishing of silica substrates, comprising: water, submicron abrasive particles, and a silica protecting agent.

25           According to the invention, a method is provided for chemical-mechanical polishing of silica substrates with a polishing slurry comprising: water, submicron abrasive particles, and a silica protecting agent.

**Embodiments of the invention will now be described by way of example.**

It has been found that the oxide removal rate decreases when an agent is present that is capable of forming an insoluble or nearly insoluble silicate. The surface, therefore, of a silica substrate can be protected by the presence of a species that forms an insoluble or nearly insoluble silicate with or on the silica surface. It is presumed that such species remains in contact or in close proximity to the oxide surface in order to protect it. Thus,

the presence of a silica protecting agent in a slurry for CMP has been found to reduce the oxide removal rate.

A silica protecting agent, as used herein, can be a submicron abrasive particle, an oxidizing agent, an additional additive, or a combination of two or more of these components. A silica protecting agent is an agent capable of forming a silicate which is other than a water soluble silicate. A water soluble silicate, as defined herein, is a silicate whose solubility in cold water (g/100 mL) is greater than 0.01. Preferably, the silica protecting agent is capable of forming a silicate having a solubility less than 0.01 g/100mL. More preferably, the silica protecting agent is capable of forming a silicate having a solubility less than 0.001 g/100mL. Even more preferably, the silica protecting agent is capable of forming a silicate having a solubility less than 0.0001 g/100mL. Still more preferably, the silica protecting agent is capable of forming a silicate which is insoluble in water. Another way of describing a silica protecting agent, as used herein, is an agent which forms a silicate upon contact with silica, wherein the formed silicate is capable of remaining on or near the silica surface thereby protecting it from polishing, erosion, or both. Contact of the silica protecting agent and silica meaning the contact which occurs throughout the entire polishing process.

An aqueous non-ferric slurry is provided which is useful for the chemical-mechanical polishing of silica substrates, comprising: water, submicron abrasive particles, and a silica protecting agent.

A non-ferric method is provided for reducing silica erosion during chemical-mechanical polishing of silica substrates using a polishing slurry comprising: water, submicron abrasive particles, and a silica protecting agent.

A silica protecting agent, as used herein, can be a submicron abrasive particle, an oxidizing agent, an additional additive, or a combination of two or more of these components. A silica protecting agent is an agent capable of forming a silicate which is other than a water soluble silicate.

The slurries of the present invention may contain an oxidizing agent (which may or may not be a silica protecting agent). Useful oxidizing agents include any water soluble

composition capable of receiving an electron from the metal atoms at the surface of the substrate during the polishing operation. By receiving electrons from the metal surface of the substrate, the oxidizing agent can transform metal atoms at the substrate surface into water soluble anions. In this way, the oxidizing agent promotes a type of dissolving of the metal into the slurry's aqueous medium. Useful oxidizing agents include acids, salts, peroxides and the like. Ordinary skill and experimentation may be necessary in selecting an oxidizing agent, depending upon the polishing system and substrate chosen. Preferred oxidizing agents would generally include: nitrates, sulfates (including persulfates), iodates (including periodates), hydrogen peroxide and/or acid derivatives thereof.

Preferred particles of the present invention are readily dispersible in an aqueous medium. The particles preferably have a surface area ranging from about 40, 60, 80, 100, 150, 200 m<sup>2</sup>/g to about 250, 300, 350, 400, 430 m<sup>2</sup>/g, and an aggregate size distribution less than about 1.0 micron, a mean aggregate diameter less than about 0.4 micron. The particles of the present invention are metal oxides selected from silica, alumina, ceria, zirconia and/or derivatives thereof and optionally can further include second metal oxide. The slurries of the present invention can be stable, but are more preferably meta-stable.

Slurries of the present invention may also comprise complexing agents which include compounds having at least two acid moieties present in the structure which can affect complexation to the target metal, such as, titanium. Acid moieties are defined as those functional groups having a dissociable proton. These include, but are not limited to, carboxyl, carboxylate, hydroxyl, sulfonic and phosphonic groups. Carboxylate and hydroxyl groups are preferred, as these are present in the widest variety of effective species. Particularly effective are structures which possess two or more carboxylate groups with hydroxyl groups in an alpha position, such as straight chain mono- and di-carboxylic acids and salts including, for example, malic acid and malates, tartaric acid and tartarates and gluconic acid and gluconates. Also effective are tri- and polycarboxylic acids and salts with secondary or tertiary hydroxyl groups in an alpha position relative to a carboxylic group such as citric acid and citrates. Also effective are compounds containing a benzene ring such as ortho, di- and polyhydroxybenzoic acids and acid salts, phthalic

acid and acid salts, pyrocatecol, pyrogallol, gallic acid and gallates and tannic acid and tannates. The most preferred complexing agents of the present invention will tend to complex with metal anions, forming a 5 or 6 member ring, whereby the metal atom forms a portion of the ring. Silicates which are insoluble or have a solubility (g per 100mL) less than 0.01 include aluminum silicate, bismuth silicate, cadmium silicate, calcium silicate, cobalt silicate, iron silicate, lead silicate, lithium silicate, magnesium silicate, manganese silicate, hydrogen silicate (silicic acid), strontium silicate, thorium silicate, zinc silicate, or zirconium silicate. Thus, a silica protecting agent would be an agent capable of forming one of these silicates upon contact with the silica surface during the polishing process.

10       Oxidizing agents in compositions of the present invention may be comprised of nitrates, iodates, perchlorates, sulfates, peroxides, or any other commonly known oxidizing agent. Counter-ions such as sodium, lithium, calcium, potassium, ammonium, and magnesium can be used. Generally oxidizing agents are used in slurries for CMP at about 1, 2, 3, 4, 5, 6, 7, 8, 9, to 10% by weight. Preferably, the oxidizing agent is present at about 2, 3, 4, 5, 6, to 7% by weight. Preferably, the oxidizing agent is other than hydrogen peroxide and a ferric oxidizer (e.g., ferric nitrate, ferric sulfate, ferric chloride, and ammonium ferrate).

20       Oxidizing agents can be classified into two types: (1) agents which can form insoluble or nearly insoluble silicates, and (2) agents which are incapable or nearly incapable of forming insoluble or nearly insoluble silicates. Type (1) oxidizing agents include iodic acid, lithium iodate, calcium iodate, silver iodate, ammonium iodate, and lead iodate. Type (2) oxidizing agents include potassium iodate, hydrogen peroxide and ferric nitrate..

25       Potassium iodate is a preferred oxidizing agent when alumina or zirconia are used as submicron abrasive particles. More preferably, potassium iodate is present at about 2, 3, or 4% by weight. Even more preferably potassium iodate is present at about 3% by weight.

      Iodic acid is a preferred oxidizing agent when a type (2) particle [type (2) particles are discussed later in the present specification] is present, especially titania. It has been

found that the use of iodic acid provides a slurry which sufficiently oxidizes the metal surface being polished while providing a decreased oxide removal rate when compared with potassium iodate. Preferably, the iodic acid is present in the slurry in an amount greater than 0% by weight and less than about 1.8% by weight. More preferably, the iodic acid is present at about 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, or 1.7% by weight. Even more preferably, the iodic acid is present at about 1.5% by weight.

When a two step polishing process is being used, the preferred amount of iodic acid present depends on the step. In the first step, the iodic acid is preferably present in an amount greater than 0% by weight and less than 1.8% by weight. More preferably in the first step, the iodic acid is present at about 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, or 1.7% by weight. Even more preferably, the iodic acid is present at about 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, or 1.7% by weight. Still more preferably, the iodic acid is present at about 1.5% by weight.

In the second step of the two step polishing process, the iodic acid is present in the slurry in an amount less than 1.8% by weight. Preferably, in the second step the iodic acid is present in an amount less than 1% by weight. More preferably, in the second step the iodic acid is present in an amount less than 0.5% by weight. Even more preferably, in the second step the iodic acid is present in an amount less than 0.1% by weight.

The submicron abrasive particles in the compositions of the present invention may be comprised of any of the oxides used for chemical-mechanical polishing such as, alumina, silica, ceria, titania, and zirconia. These particles can be classified into two types: (1) particles capable of forming insoluble or nearly insoluble silicates (e.g., alumina and zirconia) and (2) particles incapable or nearly incapable of forming an insoluble or nearly insoluble silicate. When a type 1 particle is used, then no other silica protecting agent is required. A second or third silica protecting agent can be used in combination with a type 1 particle. When a type 2 particle is used, then a silica protecting agent is required. The silica protecting agent can be selected from an oxidizing agent, another additive, or a type 1 particle (i.e., a combination of type 1 and type 2 particle). Generally the total amount of

abrasive particles used in slurries of the present invention is about 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, or 15% by weight. When the submicron abrasive particles are fumed silica, then they are preferably present at about 4, 5, 6, 7, 8, 9, or 10% by weight, even more preferably about 7% by weight. When the submicron abrasive particles are colloidal silica, then they are preferably present at about 4, 5, 6, 7, 8, 9, or 10% by weight, even more preferably about 8.5% by weight. Preferably, the submicron abrasive particles of the present invention are absent of an organic solubility coating (e.g., a phthalate compound coated thereon).

Alumina particles have been found to form aluminum silicate. Aluminum silicate is an amphoteric species which associates with the silica surface. Thus, the aluminum silicate, once formed, tends to stay on the silica surface and protect it. Consequently, alumina is a preferred abrasive particle. Preferably, the alumina is present at about 1, 2, 3, 4, 5, 6, to 7% by weight, even more preferably 2, 2.5, 3, 3.5, 4, to 4.5% by weight, still more preferably about 3% by weight.

Alumina is an abrasive particle that is available in many different forms (e.g., alpha-alumina, gamma-alumina, delta-alumina, and amorphous (non-crystalline) alumina). Preferably,  $\alpha$  and  $\gamma$  alumina particles are present when alumina particles are used. When both types of alumina are present, the  $\gamma$  alumina is preferably present in about 0.5, 1, 2, 3, 4, to 5 weight percent, more preferably from about 1, 2, 3, to 4 weight percent and even more preferably from about 2, 2.25, 2.5, 2.75, to 3 weight percent. A particularly preferred concentration of  $\gamma$  alumina is about 2.4% by weight. When both types of alumina are present, the  $\alpha$  alumina is preferably present in about 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 2, 3, 4, to 5 weight percent, more preferably from about 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, to 1 weight percent and even more preferably from about 0.4, 0.5, 0.6, 0.7, to 0.8 weight percent. A particularly preferred concentration of  $\alpha$  alumina is about 0.6% by weight.

For slurries containing titania and alumina particles, the amount of titania is preferably present in an amount of about 0.05, 0.1, 0.25, 0.5, 0.75, 1, 1.5, to 2 weight percent, more preferably between about 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, to 1

weight percent, and even more preferably from about 0.2, 0.3, 0.4, to 0.5 weight percent, and still more preferably about 0.3% by weight.

When titania and alumina particles are both present, then preferably from about 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, to 20 weight percent of the particles present in the composition are titania, from about 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, to 20 weight percent of the particles present in the composition are  $\alpha$  alumina, and from about 60, 65, 70, 75, 80, 85, 90, 95, to 98 weight percent of the abrasive submicron particle present in the composition is  $\gamma$  alumina. More preferably, about 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, to 15 wt.% of the abrasive submicron particle present in the composition are titania, about 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, to 15 wt.% of the abrasive submicron particle present in the composition are  $\alpha$  alumina, and about 70, 75, 80, 85, to 90 wt.% of the abrasive submicron particle present in the composition are  $\gamma$  alumina. Even more preferably, about 10% by weight of the abrasive submicron particles present in the composition are titania, about 10% by weight of the abrasive submicron particles present in the composition are  $\alpha$  alumina, and about 80% by weight of the abrasive submicron particles present in the composition are  $\gamma$  alumina.

It has been found that a more uniform particle size provides greater erosion protection. Thus, it is preferred that substantially all of the alumina particles are all less than about  $5\mu$ . Substantially, as used in this instance is intended to mean at least 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 99.5, 99.9% of the alumina particles are less than about  $5\mu$ .

Alumina is often prepared via milling. The milling process, unfortunately, results in milling medium being present with the alumina particles. The milling medium can be seen under a transition electron microscope to be fractured chunks. Alumina particles, in contrast, appear to be more rounded under the transition electron microscope. Milling medium, due to its fractured shape, can cause undesirable scratching, gouging, scoring, etc... during CMP. It is therefore preferable to remove the milling medium from the alumina particles prior to use in CMP slurries. Preferably, the alumina used in the present invention has been passed at least once through a  $5\mu$  filter. It is preferred that the majority of the slurry is passed through the filter 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 times. Majority, as



used here, is preferably 95, 96, 97, 98, 99, 99.5, or 99.9 wt.% of the alumina particles. It has been found that such filtering increases the copper removal as compared with unfiltered alumina.

5 It is preferable that the alumina particles be substantially free of the milling medium. Substantially free is intended to mean that 95, 96, 97, 98, 99, 99.5, or 99.9wt.% of the submicron particles are alumina. Preferably, about 95wt.% of the submicron particles are alumina, more preferably, 96wt.%, even more preferably 97 wt.%, still more preferably 98wt.%, further preferably 99wt.%, even further preferably 99.5wt.%, and still further preferably 99.9wt.%.

10 The preferred complexing agents of the present invention are a class of compounds, having at least two acid moieties present in the structure which can effect complexation to the target metal anion. Preferably, the pKa of the first acid species is not substantially larger than the pH of the polishing solution. "Substantially" is intended to mean about 1 unit (pKa or pH). Compounds which act as complexing agents or chelating  
15 agents for SiO<sub>2</sub> are described in great detail in U.S. 5,391,258 and U.S. 5,476,606, the contents of which are herein incorporated by reference.

Acid species are defined as those functional groups having a dissociable proton. These include, but are not limited to, carboxyl, carboxylate, hydroxyl, sulfonic and phosphonic groups. Carboxylate and hydroxyl groups are preferred as these are present in  
20 the widest variety of effective species.

Particularly effective complexing agents of the present invention have a structure which possess one or more carboxylate groups with hydroxyl groups in an alpha position, such as straight-chain mono- and di-carboxylic acids and salts including, for example, malic acid and malates, tartaric acid and tartrates and gluconic acid and gluconates. Also  
25 effective complexing agents are tri- and polycarboxylic acids and salts with secondary or tertiary hydroxyl groups in an alpha position relative to a carboxylic group such as citric acid and citrates. Also effective complexing agents are compounds containing a benzene ring such as ortho di- and polyhydroxybenzoic acids and acid salts, phthalic acid and acid salts, pyrocatechol, pyrogallol, gallic acid and gallates and tannic acid and tannates. The

reason for the effectiveness of these compounds is believed to lie in the extensive electron delocalization observed in the structures. This delocalization leads to a high degree of stability for the conjugate base in solution, as evidenced by the low pKa values:

Tartaric acid:  $pK_{a1} = 3.02$

5 Citric acid:  $pK_{a1} = 3.1$

Phthalic acid:  $pK_{a1} = 2.95$

The pKa limitations set forth in the present invention are due to the requirement that the free anion or conjugate base must be present in reasonable concentration for the complexing effect to occur. At  $pH \ll pK_a$  little free anion is present. At  $pH = pK_a$ , the acid is 50% dissociated. At  $pH \gg pK_a$ , essentially all of the acid is present as the anion. Thus the dissociation constant must be chosen to reflect the range of pH values normally encountered in polishing. Ideally, the pH of the polishing composition should be equal to or greater than a value equal to the  $pK_{a1}$  of the additive used for silica rate suppression. If the  $pK_{a1}$  of the additive is substantially greater than the composition pH, insufficient free metal anion is produced in solution and the advantageous complexing effect is inhibited. Thus additives such as tartaric, citric and phthalic acid ( $pK_{a1} \leq 3.1$ ) should be effective over a pH range corresponding to the normal pH range encountered in polishing metals (pH about 4-11) and would be preferred. In contrast, addition of pyrocatechol ( $pK_{a1} \approx 10$ ) would only be useful at very high solution pH and would have a more restricted utility.

20 The complexing agents in accordance with the present invention are preferably used in concentrations of from about 1, 2, 3, 4, 5, 6, 7, 8, 9, to 10 weight percent, more preferably about 2, 3, 4, 5, 6, to 7 wt.%. Preferably, the complexing agent is malic acid, tartaric acid, gluconic acid, glycolic acid, citric acid, phthalic acid, pyrocatechol, pyrogallol, gallic acid, or tannic acid. More preferably, the complexing agent is citric acid. Another 25 more preferred complexing agent is glycolic acid. Preferably, citric acid is present in a concentration of about 1, 1.5, 2, 2.5, to 3 wt.% and more preferably about 2.0 wt. %. Preferably, glycolic acid is present in a concentration of about 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, to 5 wt.% and more preferably about 3.0 wt. %. Complexing agents may be used in the compositions of this invention individually or in combinations of two or more. Preferred

complexing agents of the present invention will tend to complex with metal anions, forming a 5 or 6 member ring, whereby the metal atom forms a portion of the ring.

Features being used on substrates today are often around  $5\mu$ . However, new technologies are allowing the size of features to decrease to about  $0.18\mu$ . Such newer, smaller features, will require more sophisticated and specialized slurries. The present method of polishing is preferably performed on a substrate with features of about 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45 to  $0.5\mu$ . More preferably, the present method is performed on a substrate with features of less than  $0.4\mu$ , even more preferably, less than  $0.3\mu$ , still more preferably, less than  $0.2\mu$ , and still further preferably about  $0.18\mu$ .

Improvements in wafer manufacturing has led to an increase in feature density. Just as smaller features will require more specialized slurries, so will higher density features. The present method of polishing is performed on a substrate containing tungsten features with a density of greater than 15%, more preferably greater than 20%, and even more preferably greater than 25%. The present method of polishing is preferably performed on a substrate containing copper features with densities up to 60%, more preferably up to 90%, and even more preferably up to 95%.

Substrates which can be polished using slurries of the present invention are comprised of silica and a layer of at least one metal selected from aluminum, copper, and tungsten. Often times a barrier layer or film is used between the aluminum, copper or tungsten and the silica. The barrier layer is preferably at least one layer comprised of titanium, titanium nitride, tantalum, and tantalum nitride. Alternatively, two different barrier layers can be used, preferably titanium/titanium nitride or tantalum/tantalum nitride. A preferred substrate is one wherein a copper layer is separated from the silica substrate via a tantalum layer. Another preferred substrate is one wherein a copper layer is separated from the silica substrate via tantalum and tantalum nitride layers. Another preferred substrate is one wherein a tungsten layer is separated from the silica substrate via a titanium layer. Another preferred substrate is one wherein a tungsten layer is separated from the silica substrate via titanium and titanium nitride layers.

The slurries in accordance with the present invention can be colloiddally stable or meta-stable. When a slurry is agitated into a uniform dispersion, then placed at rest, a stable slurry will tend to stay uniformly dispersed. Perhaps a very thin line of decantant might form at the very top of the slurry after several days or so, but fundamentally the particles generally remain well dispersed throughout at least 90% of the slurry, even after  
5 being at rest for more than two weeks.

On the other hand, metastable slurries of the present invention will immediately start to fall out of suspension when at rest. Typically within a few hours (of being at rest), a large line of decantant will tend to form at the top of the slurry. Within 48 hours (of  
10 being at rest), as much as 80% or more of the slurry particles will tend to be located in the bottom two thirds of the slurry, and after being at rest for more than two weeks, the slurries of the present invention will generally have over 80% of the slurry particles located in the bottom half of the slurry.

The meta-stable slurries of the present invention are not unstable, but rather  
15 (unlike an unstable slurry), the particles will agglomerate and fall out of suspension when the slurry is at rest, but then, will immediately de-agglomerate and redisperse with simple agitation. In comparison, an *unstable* slurry will NOT readily de-agglomerate and re-disperse with simple agitation, because unstable slurries will form stage 2 agglomerates (stage 1 and stage 2 agglomeration is further defined below).

Agglomerates have generally been considered undesirable for polishing. However, agglomeration occurs in two stages, and Applicant has discovered that only stage 2 agglomeration causes the predominant undesirable effects upon chemical mechanical polishing performance. The metastable slurries of the present invention will generally not form stage 2 agglomerates, but rather will substantially only form stage 1 agglomerates.  
20 Unlike stage 2 agglomerates, stage 1 agglomerates will readily de-agglomerate with simple agitation (e.g., vigorous shaking of the slurry for about 5 seconds or less).

Stage 1 agglomeration involves agglomerated particles held together primarily by van der Waal forces. Stage 2 agglomeration can occur after stage 1 agglomeration, wherein the particles then fuse together over time, causing the particles to be primarily

held together not by van der Waal forces, but rather covalent (or similar-type high energy) bonding between the particles. The slurries of the present invention comprise an appropriate amount of ionic species and/or other adjuvants which diminish or otherwise prevent stage 2 agglomeration.

5       The ionic species used in the present invention are adjusted to diminish, inhibit or otherwise disrupt any charge layer around each particle in the slurry. For example, the anionic species in the aqueous medium will interact with, diminish or otherwise disrupt any positively charged layer around any particle, and the cationic species in the aqueous medium will interact with, diminish or otherwise disrupt any negatively charged layer  
10       around any particle.

      This disruption of any charge layer around each particle substantially removes or diminishes electrostatic repulsion between particles. Such diminished electrostatic repulsion de-stabilizes the slurry and enables the particles to move sufficiently close to one another to induce a van der Waals bond between the particles, thereby creating stage 1  
15       agglomerates. Stage 1 agglomeration may also involve hydrogen bonding between particles. A critical feature of the present invention is the *absence* of a force sufficient to repel and overcome the van der Waals forces between the particles, and therefore the slurries of the present invention will (when at rest) readily form stage 1 agglomerates and (partially or wholly) fall out of suspension.

20       During agglomeration, particles are able to move sufficiently close to one another to induce van der Waals bonds, and these bonds bias the particles together. While the particle are biased together by van der Waals forces, a second stage of agglomeration can then occur. This second stage involves bridging between the particles. Bridging occurs due to the equilibrium reactions between the particle surface and the aqueous medium  
25       surrounding the particles. The surface of the particle will tend to dissolve into the aqueous medium, then precipitate onto the particle(s). When the precipitate bridges between two particles, thereby covalently bonding the particles together, this becomes stage 2 agglomeration.

For example, although alpha alumina is generally inert (i.e., tends to resist dissolving) in an aqueous medium, conventional alpha alumina has about 1 weight percent (or more) of gamma alumina. The gamma alumina is far less inert in an aqueous medium and will typically (reversibly) dissolve, creating  $\text{AlO}_2^-$  in a basic medium and  $\text{Al}^{+3}$  in an acidic medium. In either case, the reaction is reversible and the ions which dissolve from the particle will re-deposit back onto the particle(s).

When van der Waal forces bias two particles together, this re-depositing (of the dissolved alumina back onto the particles) can cause bridging between the two particles. Indeed, by dissolving and re-forming, the two particles tend to slowly fuse together into a single rigid mass. Over time, the agglomerates will be so rigidly fused together that a hard dense sediment (of stage 2 agglomerates) is formed. Stage 2 agglomerates generally cannot be effectively broken down into their original particles, except by the application of high energy, e.g., milling or high shear mixing.

The invention recognizes that only this bridging (stage 2 agglomeration) is harmful to the polishing performance of a metal slurry. Applicant has further discovered that if such bridging is inhibited or wholly prevented, dramatically improved polishing performance can occur, even if the particles undergo stage 1 agglomerating (i.e., agglomeration substantially free of bridging) due to van der Waal forces between particles. This is preferably done by adjusting the slurry chemistry to obtain the desired state, e.g., an optimal ionic strength.

Without bridging, agglomerated particles will readily de-agglomerate with minimal agitation. Indeed, van der Waal forces are extremely weak, arguably the weakest forces which can exist between two separate bodies of matter. Without bridging, these van der Waal forces (and any hydrogen bonding between the particles) are easily overcome, and any agglomeration is not detrimental to polishing. Agglomeration without bridging will generally cause a slurry to form a fluffy "cloud" or layer toward the bottom of a slurry container, once left undisturbed for a period of time. With only minimal agitation, the cloud of agglomerates readily break apart and re-disperse in the medium. Typically, vigorous shaking of the container for less than a minute (more preferably less than 30

seconds, yet more preferably less than 15 second and yet more preferably in less than 5 seconds) will de-agglomerate the slurries of the present invention and cause the particles to uniformly disperse within the aqueous medium.

A further critical feature of the present invention is the inhibition or prevention of stage 2 agglomeration, after stage 1 agglomeration. This is accomplished by the incorporation of appropriate ionic species or other adjuvants which inhibit the fusing of stage 1 agglomerated particles into stage 2 agglomerated particles.

In a preferred embodiment, stage 2 agglomeration is inhibited by coating particles with a surfactant or polyelectrolyte prior to incorporating the particles into a slurry system. Alternatively, the surfactant or polyelectrolyte can be incorporated onto the particles after the particles are incorporated into the slurry system. The surfactant and/or polyelectrolyte will tend to remain in close proximity to the slurry particles, thereby sterically hindering the particles from coming sufficiently close to one another to enable bridging or stage 2 agglomeration. It has been surprisingly discovered that stage 1 agglomeration can occur even in the presence of surfactant or polyelectrolyte at the surface of the particles, and that the presence of the surfactant or polyelectrolyte will keep the particles sufficiently apart to inhibit or prevent stage 2 agglomeration.

Stage 2 agglomeration can also be inhibited by the use of complexing agents which inhibit deposition or sedimentation from the aqueous medium onto the agglomerated particles. Useful complexing agents include appropriate chelating compounds, ordinary skill and experimentation may be necessary in choosing appropriate chelating agents, depending upon the type of potential sedimentation or deposition for any particular slurry system. Generally speaking, water soluble, polar organic compounds having one or more (preferably two or more) Lewis acid moieties can be advantageous as complexing agents in accordance with the present invention. Preferred complexing agents include multifunctional acid or acid-hydroxide, water soluble organic compounds, such as, citric acid.

Stage 2 agglomeration can also be inhibited by modifying the solubility of "potential bridging" materials in the slurry (material in the slurry which is capable of

deposition or sedimentation). Possible modifications may include pH modification, temperature modification, ionic strength modification and the like. Ordinary skill and experimentation may be necessary to determine the appropriate modification, depending upon the particular slurry system selected.

5           Sonification is a method that can be used to determine whether agglomerates are stage 1 agglomerates (stage 1 agglomerates are agglomerates which are held together primarily only by Van der Waal forces, e.g., no bridging) or stage 2 agglomerates (stage 2 agglomerates are agglomerates which are held together by Van der Waal forces and also by bridging). Generally speaking conventional, low energy sonification will break up stage  
10   1 agglomerates but not stage 2 agglomerates. Any agglomeration of the present invention (due to the slurry being at rest for a period of time, e.g., 2 hours or more) is principally stage 1 agglomeration. Hence, the agglomerated particles of the present invention are de-agglomerated by sonification. De-agglomeration can be measured by taking a particle size distribution before and after sonification. After sonification, the size distribution should  
15   shift, thereby showing smaller particles. Thereafter, the slurry (when at rest) will tend to once again (stage 1) agglomerate.

          The stage 1 agglomerates of the present invention are stable, and stable is intended to mean that the stage 1 agglomerates will resist stage 2 agglomeration for a period of at least 3 months. Preferably, less than 15 percent (by volume) of the stage 1 agglomerates  
20   will become stage 2 agglomerates when at rest for 3 months, more preferably less than 10 percent, yet more preferably less than 5 percent, yet more preferably less than 2 percent and yet more preferably less than 1 percent of the stage 1 agglomerates will become stage 2 agglomerates when at rest for 3 months.

          The invention recognizes that particles capable of providing stage 1 agglomeration  
25   (without also causing stage 2 agglomeration) provide a superior metal polishing slurry relative to slurries having a force sufficient to repel and overcome the van der Waals forces between the particles, e.g., do not agglomerate. Hence, Applicants have found that agglomeration is not the problem, but rather bridging (e.g., the formation of hard, dense sediment) is what harms slurry performance. Not only can agglomerating slurries function



well as a metal polishing slurry, but indeed, a slurry system which enables particle agglomeration without bridging has been found to surprisingly provide improved polishing performance, particularly in the polishing of metal layers as part of the manufacture of semiconductor devices.

- 5           Stage 1 particle agglomerates generally have diminished electrostatic layer(s) and such particles tend to provide improved polishing by better interacting with the surface chemistry of a polishing substrate. Furthermore, the ionic species which inhibit or destroy electrostatic layers (around the particles) are preferably selected to provide other polishing advantages. For example, an ionic species can be used to buffer pH, provide a complexing  
10           agent to other ions in suspension (inhibit re-deposition), and/or provide selectivity (certain ionic species may protect portions of a surface, so that other portions of the surface will exhibit a higher removal rate).

- Ionic species such as acids, bases, salts, complexing agents, surfactants, electrolytes, and the like are all well known, and indeed, such ionic species are, broadly  
15           speaking, known for chemical mechanical polishing. However, it has been surprisingly discovered that when an appropriate level of ionic species is introduced into a polishing slurry (e.g., where the aqueous medium has a sufficient ionic strength), polishing performance of the slurry can be improved and unwanted particle bridging can be substantially inhibited.

- 20           The ionic strength can be adjusted by the use of agents such as acids, bases, and salts. Examples of such ionic strength adjusting agents include ammonium hydroxide, ammonium chloride, ammonium bromide, ammonium acetate, ammonium sulfate, ammonium nitrate, ammonium dihydrogenphosphate, ammonium hydrogenphosphate, ammonium benzoate, ammonium carbamate, ammonium carbonate, ammonium iodate,  
25           ammonium glycolate, ammonium citrate, iodic acid, glycolic acid, and citric acid. A preferred ionic strength adjusting agent is ammonium chloride. Preferably, the ionic strength adjusting agent is present in the slurry in about 0.01, 0.05, 0.1, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, to 5.0% by weight, more preferably about 2% by weight.

In an embodiment, the slurry's total ion concentration is greater than 0.001 molar, more preferably greater than 0.01 molar, yet more preferably greater than 0.05 molar, yet more preferably greater than 0.1 molar, yet more preferably greater than about 0.2 molar and yet more preferably greater than about 0.5 molar. In a preferred embodiment, the total ion concentration is also less than 2 molar, more preferably less than 1 molar. In a preferred embodiment, the metal oxide particles also have a maximum zeta potential greater than about plus or minus 0.10 millivolts in an aqueous medium having an ion concentration of less than 0.001 molar.

The slurries of the present invention are particularly well suited for polishing operations having high polishing surface speeds. For example, many newer polishing machines are polishing at increasingly higher revolutions per minute, and the slurries of the present invention are particularly well suited for such high speed polishing (e.g., rotary polishing speeds greater than 100 rpm, greater than 150 rpm and/or greater than 200 rpm).

The slurries of the present invention are also well suited for polishing dielectrics (silica), including low k dielectrics, such as porous silica, or organic low k dielectrics, such as fluoro polymers or copolymers.

In an embodiment, any stage 1 agglomerate transported onto the polishing interface or region will de-agglomerate or otherwise wear, rather than scratch or otherwise cause defects on the surface being polished.

In another embodiment of the present invention, the ionic strength of the slurry is adjusted after the polishing operation, thereby restoring (or increasing) the electrostatic layers around each particle. This in turn will generally cause the particles to be more easily cleaned or otherwise removed from the polished surface.

The present invention is particularly advantageous for fumed particles, since fumed particles generally have more potential sites for stage 2 agglomeration.

The slurries of the present invention comprise constituents which not only inhibit or prevent stage 2 agglomeration, but also, are sufficiently benign to the metal surface being polished to have a static metal etch rate of less than 50 Angstroms per minute, more

preferably less than 40 Angstroms per minute, yet more preferably less than 30 Angstroms per minute, yet more preferably less than 20 Angstroms per minute and yet more preferably less than 10 Angstroms per minute (up to and including 0 Angstroms per minute).

- 5        The polishing compositions of the invention can be created before or during the polishing operation. If created during a polishing operation, the polishing fluid can be introduced into a polishing interface and then some or all of the particles can be introduced into the polishing interface by means of particle release from a polishing pad. For example, a polishing pad type substrate comprising particles is described in U.S. 10 5,692,950 to Rutherford, et al. (which is hereby incorporated into this specification by reference), and in the use of such a polishing substrate during polishing, the polishing substrate will release particles, into the polishing interface which also contains a polishing fluid. As the polishing fluid and particles mix (in accordance with the present invention), they become a metastable polishing slurry, whereby the slurry will be capable of forming 15 stage 1 agglomerates without substantial formation of stage 2 agglomerates.

#### EXAMPLES

The following general polishing procedures were used:

- Wafers were polished on a Westech 372U polishing machine (available from IPEC Planar) using a IC1400 K groove primary polishing pad, a Politex Regular Embossed 20 secondary polishing pad, DF200 carrier film, TBW 100 Grit Diamond conditioner, and 150mm wafer size. The IC1400K pad was mounted to the primary platen and 20 pre condition sweeps with DI. Politex regular embossed pad was mounted to the secondary table and preconditioned with the 6" stiff bristle hand brush and DI water hand sprayer, 8 scrapes, and 8 brushes. The conditioning parameters were 7 psi DF, 3 platen sweeps (post 25 with DI Water), 70 rpm platen speed, and 75 rpm disk speed. The following polishing parameters for each phase of polishing are used (depending on the tested substrate):

Parameter	Phase 1	Phase 2 (Primary Pol Poly)	Phase 3
Time (seconds)	5	Variable	10
DF (PSI)	3	7	5
Back Press.	-3	0 (2 for Ti)	0.5
DF Ramp	5	5	5
Carrier	60	60	60
Table	60	60	60
Slurry Flow	125	125	0
Rinse	Off	Off	On

**EXAMPLE 1**

The following slurries were tested on 6" wafers containing Cu, TaN, and SiO<sub>2</sub>.

Slurry <sup>1</sup>	KIO <sub>3</sub>	CA	SSA	PVP	$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	PH
Control-a	2.0	1.0	2.0	0.2	0.6	2.4	3.6
Iodic Acid	1.0 <sup>2</sup>	1.0	2.0	0.2	0.6	2.4	3.6
Control-b	2.0	1.0	2.0	0.2	0.6	2.4	3.6

- 5 <sup>1</sup>All numbers are given in weight percentages. Water comprises the remaining weight of the slurries. CA=citric acid. SSA=sulfosalicylic acid. PVP is poly-vinylpyrrolidone, MW=10,000.

<sup>2</sup>1% HIO<sub>3</sub> was used in place of KIO<sub>3</sub>.

**Observed Metal/Oxide removal rates (Å/min)**

Slurry*	Cu	TaN	Thermal Oxide
Control-a	3290	88	163
Iodic Acid	2434	90	110
Control-b	3939	91	168

As can be seen, the presence of iodic acid surprisingly decreases the oxide removal rate as compared with a similar slurry using potassium iodate as the oxidizer.

## Claims:

1. An aqueous slurry for polishing a semiconductor substrate of silica and metal composites comprising, water, and submicron abrasive particles, characterised by;  
5 a silica protecting agent forming a silicate having a solubility in water of less than 0.01g/100mL.
2. A slurry according to Claim 1, wherein the silica protecting agent is selected from alumina and zirconia.  
10
3. A slurry according to Claim 1 further comprising an oxidizing agent.
4. A slurry according to Claim 1, wherein the silica protecting agent forms a silicate selected from aluminum silicate, calcium silicate, cobalt silicate, lead silicate, lithium  
15 silicate, manganese silicate, hydrogen silicate, zinc silicate, and zirconium silicate.
5. A slurry according to Claim 1, wherein the slurry further comprises a complexing agent.
- 20 6. A slurry according to Claim 5, wherein the complexing agent is citric acid.
7. A slurry according to Claim 5, comprising, on a weight basis: about 1, 2, 3, 4, 5, 6, 7, 8, to 9% submicron abrasive particles, about 1, 2, 3, 4, 5, 6, to 7% oxidizing agent, and about 1, 2, 3, 4, 5, 6, to 7% of complexing agent.  
25
8. A slurry according to Claim 5, comprising on a weight basis: about 3% submicron particles, about 3% potassium iodate, about 2% citric acid.

9. A slurry according to Claim 5, wherein the submicron abrasive particles are selected from silica, ceria, and titania and the oxidizing agent is selected from iodic acid, periodic acid, lithium iodate, calcium iodate, silver iodate, ammonium iodate, and lead iodate.

- 5        10. A method of polishing a substrate comprising silica, wherein the substrate is pressed against a polishing pad, the substrate and the pad are moved relative to each other, and a polishing composition is applied to the pad during the polishing operation, the polishing composition, comprising: water, submicron abrasive particles, and a silica  
10        protecting agent.

# INTERNATIONAL SEARCH REPORT

Intern 1al Application No

PCT/US 00/25222

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C09G1/02 C09K3/14 H01L21/321

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09G C09K H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 786 504 A (FUJIMI INC.) 30 July 1997 (1997-07-30) page 6, line 10-31 examples 15-20; table 2 claims	1, 2, 4-6, 10
X	WO 97 13889 A (RODEL INC.) 17 April 1997 (1997-04-17) page 5, line 7-9; claims	1-4, 10
X	US 5 770 103 A (RODEL INC.) 23 June 1998 (1998-06-23) abstract column 2, line 23-67; example 1	1-8
X	US 5 756 398 A (RODEL INC.) 26 May 1998 (1998-05-26) claims	1-8
	-/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents:

\*A\* document defining the general state of the art which is not considered to be of particular relevance

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\*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

\*O\* document referring to an oral disclosure, use, exhibition or other means

\*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*Z\* document member of the same patent family

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# INTERNATIONAL SEARCH REPORT

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

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